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NEW FERTILIZER MATERIALS

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INTRODUCTION

Before man learned how to convert the nitrogen of the air into compounds on a commercial scale our principal nitrogenous fertilizer materials were various organic wastes, sodium nitrate, and ammonium sulphate. Nitrogen, furthermore, cost us about four times as much per pound as did phosphoric acid and potash. The fixation of atmospheric nitrogen, however, has given us many new nitrogenous fertilizer materials and has appreciably lowered the cost of nitrogen in comparison with that of the other two fertilizing elements. This decrease in the cost of nitrogen is apparent not only in the price of the new nitrogenous materials but also in the materially lowered prices for sodium nitrate and ammonium sulphate, brought about by the competition of the fixed-nitrogen products.

COMMERCIAL METHODS OF NITROGEN FIXATION

Three methods of fixing atmospheric nitrogen have attained commercial importance. In the first method, the arc process, air is passed through an electric arc. Under the influence of the high temperature of the arc the nitrogen of the air combines with the oxygen to form oxides of nitrogen. These oxides are gases and can not be used directly as fertilizer. They are, therefore, converted into various solid nitrates by treatment with other compounds. In the second method, the cyanamide process, lime is first made to react with coke at a high temperature to give the compound calcium carbide. Gaseous nitrogen, obtained by separation from the air, is then brought into contact with the calcium carbide at elevated temperatures, at which a reaction takes place in which calcium cyanamide is formed. This product has found considerable use as a fertilizer. The third method is known as the synthetic ammonia process. This is the newest of the nitrogen-fixation processes, but it has outstripped the other two in commercial importance. It is, in fact, the only method that has attained commercial development in the United States. In this process gaseous nitrogen is made to combine directly with hydrogen gas to form ammonia. This is done by passing a mixture of the gases in proper proportion, at high temperatures and under pressure, over a catalyzer. The gaseous ammonia that is produced may then be liquified, while still under pressure, by cooling. The liquid ammonia is customarily called anhydrous ammonia to distinguish it from ammonia that has been dissolved in water, which is known as aqua ammonia.

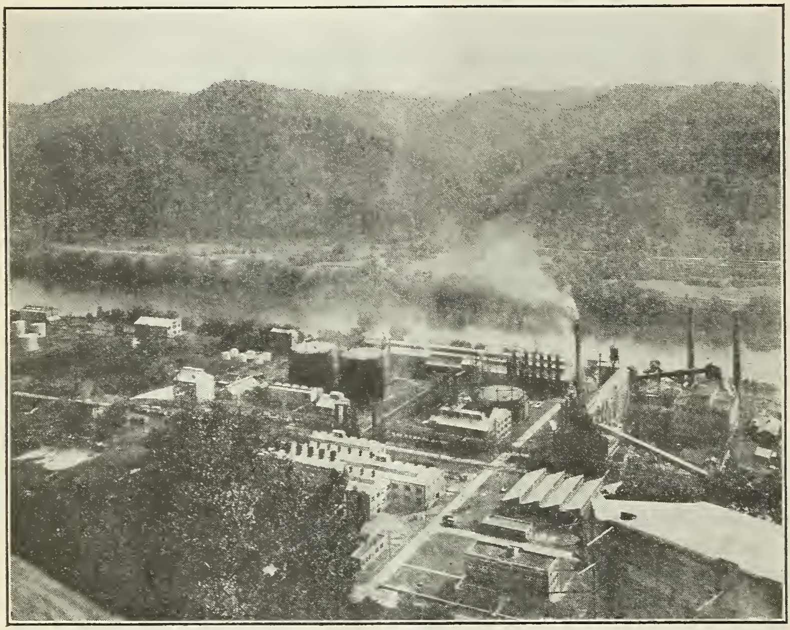

FIGURE 1.—An American synthetic ammonia plant

With the successful development of the synthetic ammonia process, ammonia has become the cheapest form of combined nitrogen, and its direct addition to superphosphates or superphosphate mixtures constitutes the most economical way of incorporating nitrogen in a mixed fertilizer. It can not, however, be used directly as a fertilizer and must be caused to combine with other compounds to form solid salts, as in the case of the oxides of nitrogen produced by the arc process, or be converted into other nitrogenous compounds.

INCREASE IN PLANT-FOOD CONCENTRATION OF FERTILIZERS

The highest concentration of available plant food in any of the organic by-products is about 18 per cent, that of nitrate of soda is 15.5 to 16 per cent, and that of sulphate of ammonia is 19.0 to 20.5 per cent. As a result of the successful fixation of atmospheric nitrogen there have appeared on the market a number of new nitrogenous fertilizer materials containing much greater percentages of plant food. Urea, for instance, contains 46 per cent of available nitrogen. As a result, also, of the combination of fixed nitrogen by various chemical processes with either potash or phosphoric acid other fertilizer materials have been produced that contain far larger concentrations of plant food than any of the materials formerly used. Thus diammonium phosphate contains 21 per cent of nitrogen and 53 per cent of phosphoric acid, that is, has a total plant-food content of 74 per cent. The general tendency following the introduction of fixed nitrogen in the fertilizer trade has been, therefore, toward the higher concentration of fertilizers. This tendency has been influenced also by the decreasing use of the organic by-products for fertilizers, owing to their greater value for feeding purposes. Whereas 58 per cent of all the fertilizer nitrogen used in 1913 was derived from natural organic sources, only 14 per cent came from these sources in 1928. As an evidence of the increasing concentration of fertilizers it may be stated that the average plant-food content in 1914 was probably less than 12 per cent, whereas in 1930 the average was probably about 17 per cent. This increase is certain to continue in the future.

The impression should not be gained from the foregoing statements that all the nitrogen-fixation products are concentrated fertilizer materials. Nitrate of soda, for example, is produced on a large scale in this country from fixed nitrogen, and calcium nitrate, which is largely produced in Norway and Germany, contains only 13 to 15.5 per cent of plant food.

Greater concentration of plant food in fertilizers has not been due solely to the introduction of the fixed-nitrogen products and the diminished use of natural organic nitrogenous materials. It has also resulted in part from the appearance on the fertilizer market of the material known as double, triple, or treble superphosphate. This material, because of its high concentration of phosphoric acid, enables its producers to enter into competition with the manufacturers of superphosphate, though the former are compelled to ship their product long distances to market. Even the average grade of the superphosphate on the market has undergone an increased concentration during the last 20 years. Although a considerable tonnage of 14 per cent superphosphate was formerly sold in this country practically all the superphosphate now produced contains at least 16 per cent of available phosphoric acid, and superphosphates with 18 and even 20 per cent of this plant-food element are on the market.

BENEFITS OF CONCENTRATION

The idea has prevailed in some quarters that concentrated fertilizers are fundamentally different from ordinary fertilizers. Such, however, is not the case. In fact, such commonly used materials as potassium sulphate (sulphate of potash) and potassium chloride (muriate of potash) contain a higher percentage of plant food than many of the new fertilizer materials and are properly classed among the concentrated fertilizer materials.

Increased concentration of the plant-food content of fertilizers offers a number of advantages to the consumer. Since a given amount of plant food is contained in a smaller weight of fertilizer, transportation charges from the manufacturer to the consumer are less, fewer bags are necessary, less storage space is required, and the labor involved in distribution on the farm is decreased. There are some disadvantages, however. For instance, on certain poor sandy soils the use of concentrated fertilizers that contain no lime and magnesia results in very little or no improvement in crop yields over those on which no fertilization is employed. It has been found that these poor results are owing to the fact that the supply of lime in the soil is inadequate to counteract the toxic action of the alkali salts in the fertilizer and to a deficiency of both lime and magnesia below the normal nutritive requirements of the plants. The addition of 10 to 30 pounds of magnesia per acre in the form of an available compound such as dolomite, magnesium sulphate, or potash salts containing magnesia and of four or five times as much lime in the form of dolomite or other liming material have been shown to overcome this disadvantage. The proportion of the special plant-food constituents such as calcium and magnesium that it is necessary to include in fertilizer mixtures intended for soils deficient in such constituents is thus seen to be relatively small. It is therefore possible to prepare highly concentrated fertilizers which contain in the same mixture a suitable proportion of all the chemical elements essential for plant growth. An analogous example of unsatisfactory results with the use of ordinary fertilizers of low concentration is shown in the case of certain soils that are deficient in manganese. Manganese salts must be applied directly to such soils or added to the fertilizer mixtures used on them in order to obtain satisfactory crop yields.

In the following pages, the more important new fertilizer materials are discussed, and brief accounts of their preparation, plant-food content, and properties are given.

NITROGENOUS COMPOUNDS

AMMONIA

The most concentrated nitrogenous material that has been used in the manufacture of mixed fertilizers is ammonia containing 82 per cent of nitrogen. Although ammonia alone can not be used directly as a fertilizer it has been employed considerably during the last three years as an addition to superphosphate, double superphosphate, and mixtures containing these phosphatic materials.

The ammoniation of superphosphate or superphosphate mixtures is a comparatively simple operation and consists merely in adding a measured quantity of anhydrous ammonia or of aqua ammonia to a weighed quantity of superphosphate or mixture in a rotating drum or standard fertilizer mixer. The ammonia is rapidly absorbed by the superphosphate, and the ammoniated material is discharged from the mixer within a few moments after the introduction of the ammonia. (Fig. 2.)

The ammonia is shipped in steel tank cars containing 50,000 pounds of liquid anhydrous ammonia. At the fertilizer plant the ammonia is used directly either from the tank car or from stationary tanks into which it has been unloaded, or it is absorbed in water to form a solution of ammonia of 25 to 30 per cent concentration before use.

AMMONIATION OF SUPERPHOSPHATES

The use of anhydrous ammonia has certain advantages over aqua ammonia. It gives a drier product which shows less tendency to stick to the stirring apparatus and other equipment in which the treated material is handled around the fertilizer plant. The quantity of ammonia in the form of a 25 to 30 per cent solution that can be added to the average superphosphate is limited to a maximum of about 2.0 to 2.5 per cent. Further additions give a mixture that is too wet and sticky. Anhydrous ammonia, however, produces dry mixtures of excellent mechanical condition up to the maximum that the superphosphate will absorb. There is apparently no difference in the chemical behavior of anhydrous and aqua ammonia in the superphosphate mixture.

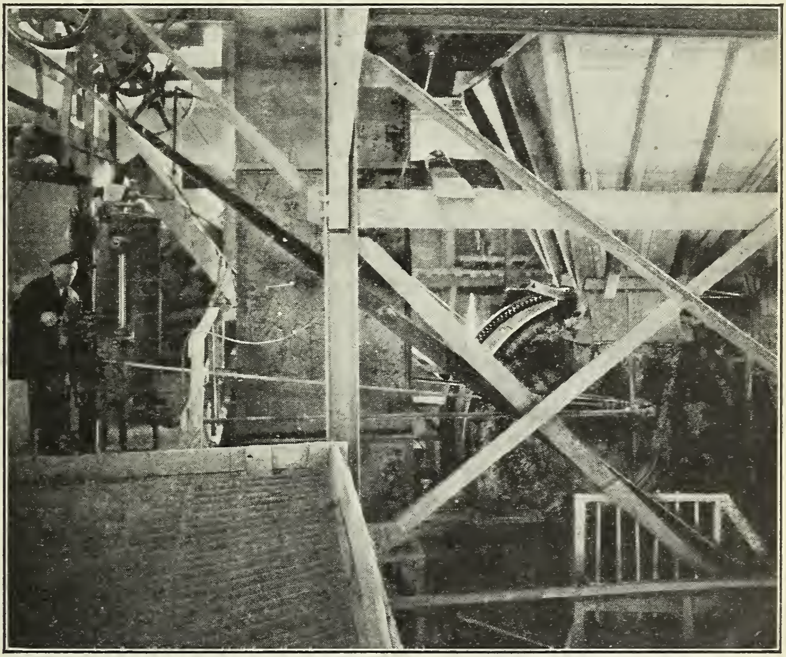

FIGURE 2.—The ammoniation of superphosphate with anhydrous ammonia, showing ammonia-measuring tank, rotating drum mixer, and feed hopper

Both forms of ammonia cause a reversion, that is, a conversion into a less soluble form, of the phosphoric acid in the superphosphate, and the maximum percentage of either that it is commercially practicable to add is considerably below the limit which the superphosphate will absorb. The actual quantity of ammonia that may be added without causing appreciable reversion to citrate-insoluble, or so-called non-available, phosphoric acid varies with the free acid present, but it is usually less than 2 per cent of the weight of the superphosphate.

The direct addition of free ammonia to superphosphates or mixtures containing superphosphate offers several advantages over its addition in the form of ammonium compounds. These advantages are: (1) Anhydrous ammonia is the cheapest form of nitrogen available to the fertilizer industry; (2) ammoniation greatly improves the mechanical condition and the drilling and storing qualities of superphosphates and fertilizers containing superphosphate; (3) the absorption of ammonia by superphosphate results in the combination of significant quantities of ammonia with a minimum dilution of the superphosphate, which is of considerable importance in the preparation of high-grade fertilizer mixtures; (4) ammoniation greatly reduces the rotting of fertilizer bags; and (5) the time required to cure the superphosphate can be reduced by using an excess of sulphuric acid in the making of the superphosphate since the excess acid is subsequently neutralized by the ammonia.

The consumption of free ammonia in fertilizer mixtures increased from about 5,000 tons in 1928 to 40,000 tons in 1930, and it is likely to increase still further in the future.

AMMONIUM SALTS

Since ammonia, with the exception of the case just discussed, can not be used directly in fertilizers it is customarily converted into various ammonium salts, such as ammonium sulphate and ammonium phosphate, or into other nitrogenous compounds, such as urea and various nitrates, suitable for fertilizer use.

AMMONIUM SULPHATE

Although the ammonium sulphate (sulphate of ammonia) on the American market is that obtained by the recovery of the ammonia in the gases from coke ovens or gas plants (called by-product ammonia) by absorption in sulphuric acid, this ammonium salt is made on a large scale in Europe by the treatment of gypsum with synthetic ammonia and carbon dioxide. In addition to the ammonium sulphate, large quantities of calcium carbonate are also obtained by this process. One of the chief uses of this material is in the preparation of Cal-Nitro, a fertilizer discussed farther on.

Ammonium sulphate prepared by the gypsum method has an advantage over the slightly acid product made from by-product ammonia in that it contains no free acid and therefore shows less tendency to cause the rotting of bags in which it is shipped. Mention is made here of this fertilizer material not because it is new but because it is another illustration of the many forms in which synthetic ammonia appears for use in fertilizers. It contains 20.6 per cent of nitrogen.

AMMONIUM CHLORIDE

The use of ammonium chloride (muriate of ammonia), a white salt containing 26 per cent of nitrogen, as a fertilizer material has not found favor in this country for two reasons; first, because of its cost; and second, because the potash salts commonly used in fertilizer mixtures contain chlorine, and the additional chlorine supplied by the ammonium chloride may increase the total content of this element in the mixture to the point where injury to crops ensues. When the chlorine in the mixture is not sufficient to cause injury, the nitrogen supplied as ammonium chloride has been found to give just as satisfactory results as that of ammonium sulphate.

In Germany ammonium chloride is produced on a large scale for fertilizer purposes from synthetic ammonia. The method used is a modification of the ammonia or Solvay process for making soda. In this process a solution of common salt (sodium chloride) is treated with ammonia and carbon dioxide to form sodium bicarbonate (cooking soda) and ammonium chloride. Instead of treating the resulting ammonium chloride solutions with lime for the recovery of the ammonia, as is customarily done, the ammonium chloride is separated from the solutions. The procedure is therefore similar to that used in the manufacture of ammonium sulphate from gypsum, ordinary rock salt being used as a hydrochloric acid carrier instead of gypsum as the sulphuric acid carrier.

POTAZOTE

When sylvinite, a natural salt consisting of both sodium and potassium chlorides, is treated in a manner similar to the Solvay process only the sodium is precipitated as sodium bicarbonate and a mixture of potassium and ammonium chlorides can be obtained from the mother liquor instead of ammonium chloride alone. Such a product of French manufacture is sold under the name potazote. Potazote is a brownish-yellow mixture containing either 12 per cent of ammoniacal ammonia and 24 per cent potash or 14 per cent of ammoniacal ammonia and 20 per cent of potash.

MONOAMMONIUM PHOSPHATE

Monoammonium phosphate is a white salt, acid in reaction, and with no tendency to become wet or cake under ordinary conditions. The processes generally used for preparing monoammonium and diammonium phosphates involve the 2-step operation of first preparing phosphoric acid and then neutralizing the acid with ammonia.

Two methods, known as the sulphuric acid or wet method and the pyrolytic or volatilization method, are in use for the commercial preparation of the phosphoric acid. In the former, phosphate rock is treated with about 50 per cent more sulphuric acid than in the manufacture of superphosphate. The phosphoric acid that is formed is then leached from the insoluble gypsum, the other product of the reaction. The maximum concentration of the phosphoric acid prepared by the wet method is 25 to 28 per cent. In the volatilization method a mixture of the phosphate rock, coke, and sand is fed into a blast or electric furnace. Phosphorus is volatilized from the mixture and, on coming into contact with the air, burns to phosphorus pentoxide, which unites with the moisture in the air to form the phosphoric acid. The acid prepared by this method may have a concentration in excess of 75 per cent. It is also purer than the crude acid prepared by the wet method, which contains considerable proportions of calcium, iron, and aluminum phosphates.

The procedure to be followed in the neutralization of the phosphoric acid with the ammonia depends on the method used in preparing the acid, that is, on its concentration and impurities, as well as on the particular ammonium phosphate to be made. The crude acid produced by the wet method is used in the preparation of both monoammonium and diammonium phosphates, whereas volatilized acid intended for fertilizer purposes is usually converted into diammonium phosphate.

The neutralizing step in the preparation of crude monoammonium phosphate from acid prepared by the sulphuric acid method consists simply in rapidly adding gaseous ammonia to the acid in open vessels until the necessary quantity has been absorbed. The calcium, iron, and aluminum phosphates of the acid precipitate out to form a slurry that is difficult to separate by filtration. The whole mass is therefore reduced to dryness by feeding it into a rotary kiln. The continuous agitation to which the material is subjected in the kiln in the process of drying yields a granular product of good drillability.

AMMO-PHOS

The fertilizer material Ammo-Phos A, having the analysis 13 per cent ammonia (10.7 per cent nitrogen) and 46 per cent phosphoric acid, is crude monammonium phosphate prepared in the way just described. Ammo-Phos B, analyzing 20 per cent ammonia (16.5 per cent nitrogen) and 20 per cent phosphoric acid, is prepared similarly by the addition of the ammonia to a mixture of phosphoric and sulphuric acids. This Ammo-Phos consists therefore of a mixture of ammonium sulphate and monoammonium phosphate.

Ammo-Phos shows little tendency to cake on storage and may actually act as a conditioner in mixtures with other fertilizer materials. It is stable at ordinary temperatures in a dry or moist condition and may be safely dried at temperatures up to 115° C. without danger of loss of ammonia.

An important modification of this process for preparing crude monoammonium phosphate has been developed commercially in Europe. In this modified process ammonium sulphate replaces somewhat less than one-third of the sulphuric acid used in treating the phosphate rock so that instead of the crude phosphoric acid a solution of monoammonium phosphate with some excess sulphuric acid is obtained. After separation from the gypsum, ammonia is added to neutralize the free acid. The final product is therefore a crude monoammonium phosphate containing some ammonium sulphate. The gypsum is used to make ammonium sulphate.

DIAMMONIUM PHOSPHATE (DIAMMONPHOS)

In the preparation of diammonium phosphate from concentrated phosphoric acid produced by the volatilization process a quantity of ammonia is absorbed in the acid, care being taken that the temperature does not rise above 90° C. After the solution has been cooled to room temperature an additional quantity of ammonia is added to precipitate the diammonium phosphate which is separated by centrifugal machines from the liquor. The production of diammonium phosphate for use as a fertilizer offers an advantage over the mono compound in that it contains 21 per cent of nitrogen and 53 per cent of phosphoric acid, whereas the latter contains only about 11 per cent of nitrogen and 60 per cent of phosphoric acid. Thus the same weight of phosphoric acid can be used to fix approximately twice the quantity of ammonia in the production of diammonium phosphate as in the formation of the monoammonium phosphate, and a corresponding economy is effected in manufacturing cost per unit of plant food. The importance of this is reflected in the increasing quantity of diammonium phosphate now being produced for fertilizer use.

It has been found that on certain sandy soils poor crop results are obtained when diammonium phosphate is used as a source of phosphoric acid. This untoward effect is apparently due to the liberation of free ammonia about the roots of the seedlings. The inclusion of a neutral calcium salt, such as gypsum, however, has been shown to control the injury very effectively. This is explained as due to the reaction between the calcium salt and free ammonia in the presence of the carbon dioxide in the soil whereby the calcium is precipitated as the carbonate and the ammonia is converted into a neutral salt.

Diammonium phosphate is a white crystalline salt, slightly alkaline in reaction, and not hygroscopic.

LEUNAPHOS

Leunaphos is a German product prepared by mixing 40 parts of diammonium phosphate with 60 parts of ammonium sulphate. It contains 20 per cent of ammoniacal nitrogen and 20 per cent of available phosphoric acid.

NITRATES

AMMONIUM NITRATE

Instead of combining ammonia as the sulphate, chloride, or phosphate, it may be oxidized and converted into nitric acid. The latter may then be neutralized with more ammonia to form ammonium nitrate. This salt should be, theoretically, an excellent fertilizer material, but its property of absorbing moisture from the air and caking to a solid mass seriously interferes with its use for this purpose. The physical properties of ammonium nitrate may be greatly improved by granulation or by mixture with certain other fertilizer or nonfertilizer materials, such as ammonium sulphate and calcium carbonate. Mixtures of this kind are sold under various trade names, such as Leunasalpeter, Cal-Nitro, and Nitro-chalk.

Ammonium nitrate contains equal parts of nitrate and ammoniacal nitrogen and has a total nitrogen content of 34 to 35 per cent.

MIXTURES OF AMMONIUM NITRATE AND CALCIUM CARBONATE

Cal-Nitro, Nitro-chalk, Kalkammonsalpeter, and Calcium carbonate-ammonium nitrate are simply mixtures of ammonium nitrate and calcium carbonate. The calcium carbonate may be a by-product of certain chemical operations, as the process of making ammonium sulphate, or it may be simply ground limestone. Fertilizer material of this kind was first produced in Germany, where it is known as Kalkammonsalpeter. The German product is exported to this country under the name Cal-Nitro. A similar product manufactured in England is known as Nitro-chalk. Ammonium nitrate by itself may explode under certain conditions, but the admixture of the calcium carbonate renders it inexplosive and also greatly improves its drilling properties. The presence of by-product calcium carbonate in these mixtures has the further advantage that it supplies lime to the soil in a very fine state of subdivision.

Cal-Nitro is light green in color, being artificially colored, and it contains 20.5 per cent of nitrogen and 35 per cent of calcium carbonate. Nitro-chalk is light buff in color and contains 15.5 per cent of nitrogen and 46 to 48 per cent of calcium carbonate. The calcium carbonate in both is of by-product origin.

An American product called Calcium carbonate-ammonium nitrate has recently been prepared by granulating a mixture of ground limestone and ammonium nitrate. It is darker in color than either the German or the English product and contains 18 per cent of nitrogen and 40 to 45 per cent of limestone.

A French product, formerly called "Le Sulfonitrate de chaux et d'ammoniaque" but now termed "Ammonitre," is similar to Cal-Nitro but contains gypsum instead of calcium carbonate. The commercial product is somewhat yellow in color and contains 15.5 per cent of nitrogen and 18 per cent of lime.

LEUNASALPETER

The German fertilizer material, sold under the names of Leunasalpeter and Montansalpeter D. A. V. V., is made by mixing ammonium sulphate and ammonium nitrate in suitable proportions in the moist state. When the moisture content of the individual salts is not more than 4 per cent of their combined weights sufficient moisture evaporates when the mixture is made to give a dry product. The heat causing this evaporation is due to the formation of a compound between the salts. Because of the formation of this compound the resultant product is less hygroscopic than the ammonium nitrate, the more hygroscopic of the two salts.

The German product contains 26 per cent of nitrogen, of which three-fourths is ammoniacal nitrogen and one-fourth nitrate nitrogen. A French product of similar character, called "Le sulfonitrate d'ammoniaque," contains 25.5 per cent of nitrogen, of which 19 per cent is ammoniacal nitrogen and the remainder nitrate nitrogen.

POTASSIUM AMMONIUM NITRATE

A commercial fertilizer material, called potassium ammonium nitrate, is made by mixing ammonium nitrate with potassium chloride. The German product, known as "Kaliammonsalpeter," contains 16 per cent of nitrogen and 28 per cent of potash, whereas the French product, "Nitropotasse," contains 16.5 per cent of nitrogen and 25 per cent of potash. The hygroscopicity of potassium ammonium nitrate is considerably less than that of ammonium nitrate, its more hygroscopic component.

SODIUM NITRATE

Sodium nitrate, known as Chile saltpeter or Chilean nitrate and produced from the enormous Chilean deposits, has been used as a fertilizer material since the early days of the fertilizer industry. It is, therefore, not a new fertilizer material, but is mentioned here because it is now made in this country on a large scale from synthetic ammonia. Instead of combining the nitric acid obtained by the oxidation of the ammonia with additional ammonia to form ammonium nitrate the nitric acid is treated with soda produced by the Solvay process already mentioned in connection with the production of ammonium chloride. A very pure form of sodium nitrate, containing 16 per cent of nitrogen, is obtained by this procedure.

CALCIUM NITRATE

Nitric acid may also be treated with limestone to form calcium nitrate, known as Norwegian saltpeter. In Norway the nitric acid used in the manufacture of calcium nitrate is obtained by the arc process of fixing nitrogen. In Germany, however, where large quantities of this salt are also produced, the nitric acid used is that resulting from the oxidation of ammonia. Here, too, calcium carbonate from the gypsum process for making ammonium sulphate is used, as well as limestone, for treatment with the nitric acid, and ammonium nitrate is added to the concentrated solution of the calcium nitrate to facilitate solidification which is accomplished by spraying from a nozzle with compressed air. The product thus obtained consists of small approximately spherical particles.

Calcium nitrate, as prepared for fertilizers, has less tendency to cake than ammonium nitrate. The granulated material remains drillable indefinitely if stored in moisture-proof containers. It is a popular source of nitrogen for use on acid soils and is largely used as a substitute for Chilean nitrate. The Norwegian product contains 13 per cent of nitrogen, whereas that produced in Germany is mixed with about 5 per cent of ammonium nitrate and contains 15.5 per cent of nitrogen.

POTASSIUM NITRATE

The use of potassium nitrate (nitrate of potash) in fertilizers has always been limited although its superior qualities as a fertilizer have long been recognized. In fact, its use as a fertilizer was suggested as early as 1656. This limited use has been owing largely to its cost.

The world supply of potassium nitrate was formerly obtained by extraction with water from incrustations on the soils around habitations in tropical countries, chiefly India, Ceylon, Mexico, and Egypt.

Potassium nitrate has also been produced, as during the Crimean and American Civil Wars, in artificial saltpeter plantations to supply the great demand for its use in gunpowder. Garbage, animal refuse, and other decaying organic matter were mixed with limestone or old plaster, wetted with urine, and allowed to ferment in piles protected from the rain. After complete decomposition the piles were mixed with hardwood ashes and leached.

Many of the Chilean nitrate deposits contain from 5 to 7 per cent of potassium nitrate, and in a few instances methods have been employed for concentrating it. A considerable tonnage of material containing 20 to 80 per cent of potassium nitrate has been obtained in this way. Some of this, containing 12 to 15 per cent of potash and a nitrogen content the same as that of Chile saltpeter, has been sold for fertilizer under the name "Nitrapo."

Much of the potassium nitrate of commerce is now made by the "conversion process," in which sodium nitrate and potassium chloride undergo a double decomposition by reaction with each other, forming sodium chloride and potassium nitrate.

Potassium nitrate may also be prepared by double decomposition between calcium nitrate and potassium sulphate, calcium sulphate (gypsum) being the other product. A considerable tonnage has been produced in Germany in this way. This process was the first in which a synthetic nitrogen product (calcium nitrate) was used in the preparation of potassium nitrate.

It should be noted that the production of potassium nitrate by the two double-decomposition methods just mentioned involves the additional treatment of materials that can be used directly as fertilizer. The cost of the potassium nitrate produced in this way is greater, therefore, than that of equivalent mixtures of the materials from which it is produced.

A process recently employed in Germany consists in the treatment of potassium chloride with nitric acid. Potassium nitrate is crystallized from the solution, and the mother liquor is neutralized with ammonia to give ammonium chloride, which is likewise crystallized out.

Potassium nitrate is much less hygroscopic than other fertilizer nitrates. It contains, in pure form, approximately 13.5 per cent of nitrate nitrogen and 46 per cent of potash.

UREA AND ITS COMPOUNDS

Synthetic ammonia may be converted into compounds other than ammonium salts and nitrates. The most important of these for fertilizing purposes is urea.

Commercial urea is a highly concentrated nitrogenous fertilizer material containing 46 per cent of nitrogen which is readily transformable by hydrolysis in the soil into ammoniacal nitrogen. Theoretically it is an ideal nitrogenous fertilizer material. Practically, however, its hygroscopicity has greatly restricted its direct use for this purpose. It can be easily granulated in the form of spherical particles of uniform size and is then much more drillable than the powdered product. Urea, as shipped from Germany, is granulated and is contained in moisture-proof bags. It is sometimes sold under the trade name "Floranid."

Urea is, for the most part, made by subjecting a mixture of ammonia and carbon dioxide to high pressures at a somewhat elevated temperature. Water is also formed in the reaction, and the solution of urea is concentrated in vacuum evaporators. The molten mass is finally sprayed into a chamber, whereupon it solidifies in pellet form.

CALUREA

The new material known as Calurea is a compound of urea and calcium nitrate made by intimately mixing these materials in proper proportions and evaporating the resulting pasty mass to dryness. The commercial product contains 34 per cent of nitrogen (one-fifth as nitrate nitrogen and four-fifths as amide nitrogen) and 13 per cent of lime.

PHOSPHAZOTE

The fertilizer material known as Phosphazote is manufactured in France and Switzerland. It is prepared by first treating a suspension of calcium cyanamide (cyanamid) in water with carbon dioxide. The insoluble calcium carbonate formed is filtered from the solution of free cyanamide. Dilute sulphuric acid is added to the solution, which is then carefully concentrated at a temperature below 70° C. The concentrated solution is finally added to phosphate rock to form a superphosphate of urea. The dried product contains 15 per cent of phosphoric acid and 7 per cent of nitrogen.

PHOSPHATIC FERTILIZERS

TREBLE SUPERPHOSPHATE

When phosphate rock is treated with phosphoric acid that has been obtained by either the wet or volatilization processes a concentrated fertilizer, variously known as double, treble, or triple superphosphate, is obtained. This product, containing 45 to 47 per cent of available phosphoric acid, can be shipped considerable distances more economically than superphosphate, which contains only 16 to 20 per cent of available phosphoric acid. When properly manufactured treble superphosphate is a dry granular solid readily drillable and mixable with other fertilizer materials in the same way as superphosphate. Double superphosphate is an example of a new concentrated fertilizer material not dependent on nitrogen fixation for its production. Double superphosphate can be ammoniated in the same way as superphosphate and will absorb considerably more ammonia without serious reversion of its phosphoric acid to the nonavailable form.

In addition to the fertilizer materials described above, which contain either one or at most two fertilizing elements, there have appeared on the market in recent years complete concentrated fertilizers containing nitrogen, phosphoric acid, and potash. These complete fertilizers are sold under the trade names Nitrophoska and Ammo-Phos-Ko.

NITROPHOSKA

The name Nitrophoska is given to a series of concentrated complete mixtures of German manufacture. All the mixtures of the series contain diammonium phosphate, ammonium nitrate, and potassium chloride or potassium sulphate. The total plant-food content of Nitrophoska ranges from 50.5 to 60 per cent.

The Nitrophoskas differ from ordinary salt mixtures in that they have been subjected to a graining treatment in the process of mixing. This treatment consists in adding a hot concentrated solution of ammonium nitrate to a mixture of the other two salts and allowing all to cool with continuous stirring. A partial reaction takes place under these conditions with the formation of potassium nitrate and ammonium chloride or ammonium sulphate.

The Nitrophoska mixtures that contain ammonium nitrate and potassium chloride have a hygroscopicity between that of ammonium nitrate and sodium nitrate. Therefore they soon cake or become sticky when exposed to a humid atmosphere, and this property greatly interferes in moist climates with the drillability of the material unless it is stored in air-tight containers until drilled.

AMMO-PHOS-KO

Ammo-Phos-Ko is the name given to a series of concentrated mixtures of American manufacture. They consist of various proportions of Ammo-Phos and potassium sulphate. Monoammonium phosphate, the principal constituent of Ammo-Phos, and potassium sulphate are among the least hygroscopic of soluble salts, and mixtures of these materials are drillable at humidities which would cause most soluble fertilizers to become sticky or entirely undrillable. The total plant-food content of the Ammo-Phos-Kos ranges from 45 to 50 per cent.

SUMMARY

In this report commercial processes for fixing atmospheric nitrogen for fertilizer purposes are briefly outlined, and various factors that have played a part in increasing the concentration of fertilizers are discussed. Advantages and disadvantages of concentrated fertilizers are mentioned.

The use of ammonia, the product of the synthetic ammonia process for fixing nitrogen, in the ammoniation of superphosphate is described, and brief accounts are given of the preparation, plant-food content, and properties of the various salts and compounds into which it is converted for fertilizer purposes. A number of other fertilizer materials and mixtures are also included.

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